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AN ASPHERICAL LENS
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(54) AN ASPHERICAL LENS

SPECIFICATION /

1. Title of the Invention

AN ASPHERICAL LENS

2. Claims

An aspherical lens wherein a ultraviolet-hardening resin layer is provided in the desired form on the surface of a glass lens which serves as the parent material, said aspherical lens characterized by the fact that said ultraviolet-hardening resin layer is formed by the polymerization-hardening of a composition containing

- (A) a bi- to tetrafunctional urethane-modified polyester (meth)acrylate obtained by the reaction of diisocyanate and a (meth)acrylate having a hydroxyl group in the molecule with a polyester oligomer obtained by the reaction of a polybasic acid and a polyvalent alcohol,
 - (B) a trifunctional (meth)acrylate,
 - (C) a monofunctional (meth)acrylate, and
 - (D) a photopolymerization initiator
- by means of ultraviolet light.

3. Detailed Description of the Invention

(Industrial Field of Application)

The present invention concerns aspherical lenses which form optical systems used in the optical systems of photographic cameras,

*Numbers in the margin indicate pagination in the foreign text.

video cameras, microscopes, telescopes or optical disk pickup devices, etc., in particular aspherical lenses wherein a ultraviolet-hardening resin layer is provided in the desired form on the surface of a glass lens which serves as the parent material.

(Prior Art)

In the past, there have been many examples where an ultraviolet-hardening resin is used as the resin layer of this type of aspherical lens, but in past ultraviolet-hardening resin compositions it has been impossible to obtain good post-hardening heat resistance, moisture resistance, hardness, etc., while at the same time increasing accuracy of form in hard molding.

For example, the polyfunctional types of photohardening acrylate resins conventionally used have had good light transmittance and hardness as a resin material, and also good characteristics in high-temperature, high-humidity environments, but also have the problem of a high hardening shrinkage factor so that it is difficult to achieve accuracy of form.

Also, in recently developed ultraviolet-hardening epoxy type resins, the shrinkage factor is approx. 3%, smaller than the 9 to 8% shrinkage factor of acrylate-type resins, so that it is easy to achieve the desired accuracy of form. However, in photohardening epoxy resins, since a catalyst, etc., is used for polymerization initiation, high-temperature and high-humidity resistance characteristics are poor, and there is also the characteristic coloration of epoxy, considered to be

a factor in problems of light resistance, so that there are problems with practical application.

In order to solve the aforesaid problems in the resin materials, a lens provided with a resin layer having a double-layer structure has been conceived (Kokai No. 60-56544). This lens is formed by providing a thin film of a polyfunctional ultraviolet-hardening acrylate resin having a high shrinkage factor but having good high-temperature, high-humidity resistance on an ultraviolet-hardening acrylate resin having comparatively low shrinkage factor and thus allowing formal accuracy, but having a low hardness and highly susceptible to moisture absorption, and accordingly, poor resistance to high temperature and high humidity. This lens is provided with the better characteristics of each layer, but requires a two-stage ultraviolet-hardening process, increasing the amount of equipment, space, and time required for production, and thus increasing production costs, so that it is suitable for the production of large lots, and its range of practical application is limited.

Also, in order to solve the aforesaid problems in the resin itself, a molding method whereby pressure is applied in hardening is known. This method is one in which the interval between the parent paternal lens and the mold is compressed inward when the resin composition, which is composed of a polyfunctional acrylate, is hardened. When this method is used, the formal accuracy of the resin formed is improved, but since lower pressures are not very effective, it is necessary to apply a certain level of high compression. As a

result, there is the danger of the parent material lens breaking during processing, and the problem of the fact that this process can only be applied to lenses which use a high-strength material or thick lenses.

The present invention was produced in light of the aforesaid problems and has the purpose of offering an aspherical lens which has a small shrinkage factor without impairment of the high hardness, high resistance to high temperatures and high humidity of ultraviolet-hardening acrylate resins. Another purpose of the present invention is to offer an aspherical lens in which the surface layer (ultraviolet-hardening resin layer) has a single-layer structure and manifests excellent formal accuracy without being subjected to compression.

(Means Used to Solve the Problems)

The aforesaid purposes are achieved by means of an aspherical lens wherein an ultraviolet-hardening resin layer is provided in the desired form on the surface of a glass lens which serves as the parent material, said aspherical lens characterized by the fact that said ultraviolet-hardening resin layer is formed by the polymerization-hardening of a composition containing

- (A) a bi- to tetrafunctional urethane-modified polyester (meth)acrylate obtained by the reaction of diisocyanate and a (meth)acrylate having a hydroxyl group in the molecule with a polyester oligomer obtained by the reaction of a polybasic acid and a polyvalent alcohol,
- (B) a trifunctional (meth)acrylate,

- (C) a monofunctional (meth)acrylate, and
 - (D) a photopolymerization initiator
- by means of ultraviolet light.

Figure 1 shows the configuration of the aspherical lens of the present invention.

The aspherical lens of the present invention is formed of an ultraviolet-hardening resin layer (2) formed on a parent material (1).

The mother material is an inexpensive lens formed by the spherical polishing of normal optical glass. The ultraviolet-hardening resin layer (2) is thinner than the parent material, normally having an average thickness of 10 to 300 micrometers, and an aspherical form which is rotationally symmetrical with regard to the optical axis.

The lens of the present invention is obtained by pouring a fixed quantity of ultraviolet-hardening monomer into an aspherical mold having a transcription layer which is the reverse of the desired aspherical form, on this fixing the parent material lens surface which is to be aspherical surface facing the mold surface so as to be held in fixed interval with the mold, irradiation with ultraviolet light from the lens side, and separation of the back mold on which the monomer has been polymerized and hardened without compression.

The aspherical lens of the present invention is not limited to that shown in Figure 1 where the resin layer is provided on a convex side of the mother material; as an example of a variation, as shown in Figure 2, the resin layer may be provided a concave surface of the parent material lens, or as shown in Figure 3, may be provided on both

faces of the

lens. In addition, in order to increase the adhesion between the resin and the glass, as shown in Figure 5, the resin layer may be applied after the glass surface has been coated with a silane coupling material, etc., normally used for increasing adhesion. Also, after the resin layer has been added, as shown in Figure 6, 1, 2 or more layers such as a protective layer for moisture protection and vapor deposition layers for preventing reflection may be provided on the resin layer.

The present invention has the purpose of providing an aspherical lens, but can also be applied in the formation repeated chevron forms seen in *funerel* [phonetic] lenses, focusing plates for cameras, and beam splitters.

The components (A), (B), (C), and (D) which form the ultraviolet-hardening resin layer used in the aspherical lens of the present invention are next explained.

Component (A) has a polyester oligomer formed of a polyvalent alcohol and polybasic acid as a main chain skeleton, and this polyester oligomer is synthesized using at least a bivalent to tetravalent alcohol or a dibasic to tetrabasic acid. Isocyanato groups on one end of the diisocyanates are bonded to the hydroxyl groups on the terminal portions of the main and side chains of Component (A), and a (meth)acrylate having a hydroxyl group within its molecule is bonded with the isocyanato groups on the other end of said diisocyanate.

As the aforesaid tetrabasic acids, tetrabasic acids of pyromellitic acid anhydride, 2,3,3',4'-biphenyltetracarboxylic

dianhydride, benzophenonetetracarboxylic dianhydride, bis(3,4-dicarboxyphenyl)methane dianhydride, etc., can be used.

As the aforesaid tribasic acids, tribasic acids such as trimellitic acid; and tribasic acids obtained by the partial esterification of pyromellitic acid anhydride, 2,3,3',4'-biphenyltetracarboxylic dianhydride, benzophenonetetracarboxylic dianhydride, bis(3,4-dicarboxyphenyl)methane dianhydride, etc., can be used.

Also, as dibasic acids, phthalic anhydride, isophthalic anhydride, terephthalic anhydride, (anhydrous) succinic acid, adipic acid, azelaic acid, sebacic acid, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, hymic [sic] anhydride, maleic anhydride, fumaric acid, itaconic acid, etc., may be used.

As tri- or tetravalent alcohols, glycerin, trimethylolmethane, trimethylolethane, trimethylolpropane, pentaerythritol monoallyl ether, pentaerythritol, etc., can be used.

Also, as bivalent alcohols, ethylene glycol, propylene glycol, neopentyl glycol, diethylene glycol, dipropylene glycol, hydrogenated bisphenol A, 2,2'-di(4-hydroxypropoxyphenyl)propane, 1,3-butanediol, 1,4-butanediol, 1,5-pantanediol, 1,6-hexanediol, trimethylene glycol, triethylene glycol, pentaerythritol diallyl ether, etc., can be used.

As the aforesaid diisocyanates, trilene diisocyanate, 4,4'-diphenylmethane diisocyanate, xylylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, lysine diisocyanate, hydrogenated xylylene diisocyanate, etc., can be used.

As the aforesaid (meth)acrylate having a hydroxyl group in its molecule, 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, glycerine monoacrylate, etc., can be used.

Component (A) is obtained by reacting a polyvalent alcohol and polybasic acid to obtain a polyester oligomer, then the addition reaction of the diisocyanate, and finally the addition reaction of the (meth)acrylate.

As Component A, in addition, an isocyanate containing unsaturated groups and represented by the general formula /

(where R is hydrogen or a methyl group, R' is $-COOC_nH_{2n}$ [?] (where n is an integer from 1 to 8)) can be used. In this case, by reacting isocyanate groups with the hydroxy groups in the terminal portions of the main chain or side chains of the aforesaid polyester oligomer, a urethane-modified polyester (meth)acrylate can be obtained. Said isocyanates include, for example, 2-isocyanate-methyl (meth)acrylate, 2-isocyanate-ethyl (meth)acrylate, 2-isocyanate-propyl (meth)acrylate, 2-isocyanate-octyl (meth)acrylate, P-isopropenyl- α,α -dimethylbenzyl isocyanate, P-ethylenyl- α,α -dimethylbenzylisocyanate, m-ethylenyl- α,α -dimethylbenzylisocyanate, etc.

As the trifunctional (meth)acrylate of Component (B), trimethylolpropane tri(meth)acrylate, tri(meth)acrylate of tris(2-

hydroxyethyl)isocyanate, and tri(meth)acrylate of tris(hydroxypropyl)isocyanurate, can be cited.

As the monofunctional (meth)acrylate of Component (C), for example, methyl (meth)acrylate, ethyl (meth)acrylate, cyclohexyl (meth)acrylate, dicyclopentyl (meth)acrylate, isoboronyl (meth)acrylate, boronyl (meth)acrylate, phenyl (meth)acrylate, halogen-substituted phenyl (meth)acrylate, benzyl (meth)acrylate, α -naphthyl (meth)acrylate, β -naphthyl (meth)acrylate, cyclopentyloxyethyl acrylate, etc., can be cited.

As the photopolymerization initiator of Component (D), 1, 2 or more compounds selected from among benzophenone, hydroxybenzophenone methane sulfonate, O-benzoyl-methylbenzoate, p-benzoyl-methylbenzoate, p-chlorobenzophenone, p-dimethylaminebenzophenone, and other benzophenone substituted derivatives, benzoin and benzoin allyl ether, benzoin alkyl ethers in which the alkyl group is methyl, ethyl, isobutyl, isopropyl, etc., and other benzoin substituted derivatives, acetophenone and diethoxy acetophenone, 1-hydroxycyclohexylphenylketone, benzyldimethylketal, 2-hydroxy-2-methylpropiophenone, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropiophenone, and other acetophenone substituted derivatives, oxime compounds such as benzyl and 1-phenyl-1,2-propanedione-2-O-benzoyloxime, etc., may be used.

The condensation reaction when the polyester oligomers of the aforesaid Component (A) and Component (B) are synthesized can be performed by heating reaction using a conventional method; for example,

after adding the source materials, reaction can be performed at 150 to 250°C under agitation, and the reaction stopped when the acid value has reached the desired level. In the above, it is desirable that the proportion of polybasic acid to polyvalent alcohol used be approx. 1:2 in equivalence ratio, but this ratio will vary in accordance with the molecular weight, the residual alcohol groups, etc.

In the ultraviolet-hardening resin layer of the aspherical lens of the present invention, the aforesaid Component (A) is the ingredient which maintains the moisture resistance, heat resistance, ultraviolet light resistance, and other environmental resistance characteristics at satisfactory levels, and normally is used in an amount equivalent to 10-90 wt %, preferably 25-70 wt %. This is because if the amount used is less than 10 wt %, these environmental resistance characteristics are impaired, while if it exceeds 90 wt %, there is a marked increase in viscosity, and workability is reduced.

Component (B) is the ingredient which is used to increase hardness, thermal deformation temperature, and other physical characteristics, and normally is used in an amount equivalent to 10-70 wt %. This is because if the amount used is less than 10 wt %, no increase in hardness, etc., can be expected, while if it exceeds 70 wt %, the hardened object becomes brittle, the shrinkage factor in hardening is increased, and processing accuracy is impaired.

Component (C) is the ingredient which adjusts the balance between fluidity and viscosity, hardness, etc., when the ultraviolet-hardening resin layer of the aspherical lens of the present invention is molded,

and can be used in a proportion desired, but normally is used in an amount equivalent to 20-40 wt parts per 100 wt parts of resin composition containing Components (A) and (B). /

Component (D) is the ingredient which has the ability to begin polymerization by absorbing light which has been irradiated, and can be used in a desired proportion in accordance with the hardness, physical properties of the hardened object, etc., but normally is used in an amount equivalent to 0.5-10 wt parts per 100 wt parts of resin composition containing Components (A) through (C). /5

Publicly known polymerization accelerators, polymerization stoppers, mold release agents, surface smoothing agents, defoaming agents, etc., can be added to the ultraviolet-hardening resin layer of the aspherical lens of the present invention as necessary.

As the light source used for ultraviolet irradiation, a chemical lamp, low-pressure mercury lamp, high-pressure mercury lamp, carbon arc, xenon lamp, etc., can be used.

(Working Examples)

Next, the present invention is explained in further detail by means of working examples.

Preparation Example 1

96 g trimellitic anhydride, 228 g propylene glycol, and 111 g of phthalic anhydride were placed in a 4-neck flask equipped with a condenser, nitrogen gas introduction tube, temperature gauge, and

agitator, and were heated and agitated in a nitrogen atmosphere. After heating to 150°C the mixture was maintained at this temperature for 2 hrs., then the temperature was gradually increased and reaction was induced at 200°C, and when the acid number reached 5 or less, the reaction was terminated. After cooling to room temperature, 277 g isophorone diisocyanate, 174 g 2-hydroxyethyl acrylate, and 0.17 g dibutyltin dilaurate were added, and after 3 hrs of reaction while the reaction system was gently heated so that its temperature did not exceed 80°C, the temperature was raised to 100°C over a period of 1 hr., reaction was induced for 3 hrs., and the urethane-modified polyester acrylate (I) was obtained.

Preparation Example 2

54 g trimethylolpropane, 182 g of tetrahydronaphthalic anhydride, and 108 g of 1,3-butylene glycol were added in the same way as in Preparation Example 1, and heated and agitated in a nitrogen atmosphere. After heating to 150°C, the mixture was maintained at this temperature for 2 hrs, then the temperature was gradually increased and reaction was induced at 200°C, and when the acid number reached 5 or less, the reaction was terminated. After cooling to room temperature, 222 g isophorone diisocyanate, 156 g hydroxypropyl acrylate, and 0.14 g dibutyltin dilaurate were added, and after 3 hrs. of reaction while the reaction system was gently heated so that its temperature did not exceed 80°C, the temperature was raised to 100°C over a period of 1 hr., reaction was induced for 3 hrs., and the urethane-modified

polyester acrylate (II) was obtained.

Test Examples 1-6 of Asymmetric Lens Test Pieces

The urethane-modified polyester acrylates obtained in Preparation Examples 1 and 2 above were mixed with other components as shown in Table 1 in the mixture ratios shown in the same table, and 6 types of compositions (Compositions 1 and 2 of resin layers in accordance with the present invention and Comparative Compositions 1-4) were obtained.

These compositions were provided as spherical surface resin layers by the aforesaid methods so that the central thickness was 150 μm and $R = 41.49 \text{ mm}$ on the R1 convex surface of a parent-material spherical lens of material BK7, where $\varphi = 40.5 \text{ mm}$, $R1 = 41.34 \text{ mm}$ convex, $R2 = 203 \text{ mm}$ concave, central thickness = 11.33 mm, and 6 types of compound spherical lenses were obtained.

(1) Formal accuracy

The forms of the compound spherical lenses obtained as described above were measured by means of a Zygo [phonetic] interferometer, and from the disturbance in the interference fringes obtained the formal accuracy was calculated. The results are shown in Table 1.

(2) Hardening shrinkage factor

Based on JIS K-7112, the specific gravities before hardening (liquid state) and after hardening (the aforesaid mold-poured plate) were measured, and the numerical value obtained by dividing the difference in specific gravities by the specific gravity after hardening was made the hardening shrinkage factor.

(3) High temperature and high humidity environment resistance

characteristics

The lens obtained was exposed for 500 hrs in a high-temperature, high-humidity vessel of 70°C and 85% RH, and the external appearance, microscopic observations (x 200), formal accuracy, etc., were checked.

(4) Pencil hardness

The lens surfaces were subjected to scratch tests for every level of pencil hardness, and the maximum hardness at which scratches were not made on the resin surface was made the pencil hardness.

In Comparative Compositions 1 through 4, the formal accuracy was $\pm 1 \mu\text{m}$ or above, and changes in external appearance were observed in the high temperature and high humidity environment, and reduced hardness was observed, while in Compositions 1 and 2 using resin layers according to the present invention, formal accuracy showed a good value of $0.6 \mu\text{m}$, the lenses were suitable for use as photographic lenses, and neither changes in external appearance in the high temperature, high humidity environment nor reduced hardness were observed.

Working Example 1

An aspherical lens having the same form as that used in a commercially sold single-lens reflex camera was prepared, the form was measured using a contact-type aspherical surface measurement device, and the results obtained are shown in Figure 7. When measured at $n = 2$, in each case the maximum error was within $0.5 \mu\text{m}$, confirming that when the present resin mixture is used, an aspherical surface can be accurately formed.

TABLE 1

			Composition of Present Invention		Comparative Composition				
			1	2	1	2	3	4	
Com- po- si- tion	A	Urethane-modified polyester acrylate (I)	50	--	5	95	--	--	
		Urethane-modified polyester acrylate (II)	--	50	--	--	50	10	
	B	Trimethylolpropane trimethacrylate	20	--	50	--	--	--	
		Triacrylate of tris(2- hydroxyethyl) isocyanate	--	20	--	--	5	80	
	C	Cyclohexyl acrylate	30	--	45	5	--	--	
		Benzyl acrylate	--	30	--	--	45	10	
	D	1-hydroxycyclohexyl phenylketone	1	1	1	1	1	1	
Phys- ical Pro- per- ties	Hardening shrinkage factor (%)			5.0	5.3	7.5	Processing difficult due to viscosity	8.3	8.8
	High temperature and high humidity environment resistance			no change	no change	surface roughening		no change	surface roughenin g
	Pencil hardness			H	H	B		2B	2H
	Formal accuracy (μ)			± 0.6	± 0.6	± 1.5		± 1.2	± 2.4

(Merits of the Invention)

As explained above, the aspherical lens of the present invention has merits such as the following:

- It provides a high formal accuracy without impairment of the high hardness, high temperatures and high humidity environment resistance, hardness and other characteristics necessary in optical lenses.

- It offers an aspherical lens in which the ultraviolet-hardening resin layer has a single-layer structure, and it does not require excessive production equipment, reducing the number of production steps, along with costs, and allowing the production of small lots.

- Since the hardening shrinkage factor of the ultraviolet-hardening resin layer is small, the compression is unnecessary in hardening, it can be used in lenses of substances which are easily broken when compressed and thin lenses, and the optical design of a wide range of lens types and substances (index of refraction) is made possible.

4. Brief Explanation of the Figures

Figure 1 is a cross-sectional diagram of an aspherical lens of the present invention, Figures 2, 3, 5, and 6 are examples of other modes of the aspherical lens of the present invention, Figure 4 is a complex optical element having a repeated-chevron surface, and Figure 7 is a graph showing the measurement results of the formal accuracy of an aspherical lens.

1: parent material glass substrate
1a: substrate of complex optical element
2: aspherical resin layer
3: resin layer with repeated-chevron surface provided
4: layer of silane coupling agent, etc.
5: moisture resistance layer or antireflection layer

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7: Formal accuracy of complex aspherical lens

[keyed items]

a: Formal error

b: Center of optical axis

c: Mold

d: Design value

e: Measured value

f:

aspherical design value

mold

aspherical lens test piece (1)

aspherical lens test piece (2)

aperture: ϕ 40.5

measurement device: Contact-type aspherical surface measurement device